ON

SELENIUM

AND SOME

OF THE METALLIC SELENIETS.

INAUGURAL DISSERTATION

FOR PROMOTION TO THE DEGREE

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TO

MY HIGHLY RESPECTED INSTRUCTOR

REV. F. A. P. BARNARD L. L. D.

FORMERLY

PROF. OF CHEM. IN THE UNIV. OF ALA

NOW

PRES. OF THE UNIV. OF MI.

THESE PAGES ARE RESPECTFULLY

DEDICATED.

To my highly-honored instructor Prof. Wöhler, at whose suggestion these investigations were begun, my warmest thanks are due, for the many favors conferred on me during the year that I have spent in his Laboratory.

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I.

SELENIUM.

HISTORY.

Selenium was discovered in 1817 by Berzelius. This distinguished chemist, while engaged in an examination of the method of preparation of Sulphuric acid at Gripsholm in Sweden, found a partly red, partly light-brown sediment which before the blow pipe gave the alliaceous odor and left metallic lead. As this odor had been given by Klaproth as a sign of the presence of Tellurium, and as Gahn, who was engaged with Berzelius in the examination, had often remarked the same, near the ash receivers in Fahlun where the sulphur used in the preparation of the acid was obtained, Berzelius, curious to find so rare a metal in this brown sediment, entered into an investigation of the same in order to separate the tellurium but could find none. Thereupon he caused all the sediment which had been formed in several months during the constant burning of the sulphur from Fahlun to be collected, and subjected it to a thorough investigation; he found that it contained a hitherto unknown substance which, in its behavior, closely resembled tellurium. In order to indicate this similarity, named it Selenium from the Greck word $\Sigma\varepsilon\lambda\acute{\eta}\nu\eta$, which means moon, as Tellur is the name of the earth, considered as a planet.

The Sulphuric acid manufactory at Gripsholm (in which Berzelius was a share-holder) made use of Sulphur prepared at Fahlun from sulphuret of iron which was found in considerable quantity in the copper mines of that locality, and was generally mixed with sulphurets of lead and zinc, and other impurities. The Sulphur was obtained by roasting this ore, and was afterwards burned at Gripsholm to sulphurous acid. In the leaden chamber this came in contact with steam, air, and nitrous acid obtained by placing on the floor shallow vessels containing nitric acid. The sulphurous acid became oxidized to sulphuric, which after every operation was allowed to run off and there remained on the floor the reddish sediment.

In this sediment Berzelius found Selenium together with lead, copper, iron, tin, zinc, arsenic and quicksilver and a large quantity of Sulphur He separated the Selenium by digesting the mass with Aqua Regia, diluting and filtering. Sulphate of lead and Sulphur remain undissolved. The solution after filtering was treated with sulphuretted hydrogen which precipitated Selenium with copper, tin, arsenik and quicksilver. zink and iron remain in solution. The precipitate was again dissolved in Aqua Regia until the sulphur became pure citron yellow. The fluid was then evaporated down until the greater part of excess of acid was driven off. There remained Sulphate of copper, clorides of tin and quicksilver a small quantity of arsenious, and a large quantity of Selenious acid.

By means of a solution of caustic potassa the

oxides of tin, copper and quicksilver were precipitated. The alkaline liquid was filtered, evaporated to dryness, and heated in a platinum crucible in order to drive off traces of quicksilver. The heated mass was quickly and finely pulverised, in a warm mortar, with finely pulverised cloride of ammonium, mixed and heated by degrees. Ammonia and water were given off which contained a little selenium mechanically suspended to prevent the loss of which, they were collected in a receiver. By higher heat selenium sublimed as a black or brown powder. By this operation the selenious salt of potash is the only one that is changed. This is effected by means of the hydrogen of the ammonia, which is oxidized at the expense of the oxygen of the selenious acid, reducing it to selenium, and nitrogen is set free. The substance remaining in the retort is treated with water, which dissolves the salts and leaves selenium, which can be collected on a filter, washed, dried and distilled in a glass retort. After dissovering this element, Berzelius made numerous experiments to ascertain its qualities and combinations. As the result of these, the place, in the order of the elements, between sulphur and tellurium, was assigned to it. Mitscherlich, ten years afterwards, discovered the selenic acid, and proved that it was isomorphous with sulphuric acid. Muspratt still later published the result of his experiments with selenious acid and its salts. Wöhler, by the discovery of the combination with aethyl, introduced selenium into organic chemistry. During the last year Hofacker published

a description of the method of preparation, and manner of analysis, of a salt corresponding to the „Schlippsches Salz“ in which selenium takes the place of sulphur and gives crystals of the same form with those of the salt referred to.

These are the principal researches made in regard to this element, as, on account of its rare occurrence, few chemists have been able to obtain it in sufficient quantities. It has however lately become more common. Soon after its discovery, in the same year, Berzelius found a new mineral, whose formula he determined $= 2CuSe + AgSe^2$, and which was analogous in composition with the Silver copper glance $= 2CuS + AgSe^2$, a short time before described by Hausmann and Stromeyer.

In allusion to the fortunate circumstance of its being discovered at a time most interesting for the history of selenium, he gave it the name Eukairit (εὔκαιρος). At the same locality, namely Skrikerum, in the province Smoland, another mineral was found which consisted entirely of selenium and copper. Among the other minerals in which it occurs the following may be named; Rionite, in combination with zinc and mercury, Seleniuret of lead, of silver, of mercury in the Hartz. Seleniuret of lead and copper in Thüringen and of lead and mercury, and lead and cobalt in the Hartz mountains. Seleniuret and sulphuret of mercury at San Onofre in Mexico. (According to Del Rio it is found native at Culebras in Mexico.)

In combination with sulphur, to which it gives a red-

dish tinge, it is found one of the Lipari Islands (Vulcano) and also on the volcano Kilauea on Hawai. According to Buch and Wöhler, it is contained in the sulphuret of iron from Kraslitz in Bohemia, which is oxidized to sulphate of iron, used for prepering oil of vitriol, which, on being diluted with water, gives a precipitate of selenium Lewenau found that the sulphuret of iron from Luckawitz in Bohemia, in the preparation of sulphuric acid, left in the leaden chamber a sediment which contained 7.8 per cent. The sulphuret, from which Nordhausen oil of vitriol is prepared, as also that from Felsobanja, Rota and Kapnik, contains a small quantity. Sulphuret of copper from Paris mountains on Anglesea and that from Rammelsberg near Goslar also contain it; the latter of which deposits a sediment in the leaden chamber.

In „kupferpecherz“ and „kupferblüthe“ from Rheinbreitenbach. In Uranpecherz from Johanngeorgenstadt and Schneeberg. In sulphuret of molybdenum from Schlackenwalde. In tetradymit a small quantity is contained, for the separation of which from tellurium, Oppenheim has given the following method. The finely powdered substance is melted, with the triple amount of cyanide of potassium, in a porcelain crucible, by means of the Berzelius lamp. After cooling, the mass is almost entively dissolved in water, with a reddish purple color, and becomes by degrees colorless, on exposure to the air, and tellurium is precipitated in the form of powder, and when a larger quantity is present, as acicular crystals. The tellurium is filtered off, and, by treating the solution with hydrochloric acid, selenium is precipitated.

1.

FROM „SELEN SCHLAMM“ OR SEDIMENT.

From the sediment of Luckawitz, selenium is prepared by dissolving it in caustic potash (heated), and exposing to the atmosphere at 22° C. Hyposulphite of potassa is formed and selenium is precipitated to the amount of 11 1/4 per cent of the sediment. In order to obtain the remaining 1/4 per cent, the solution is boiled with a piece of sulphur.

Wöhler has given a method, for procuring selenium from the sediment obtained at Ocker in the Hartz, which, at the same time, gives it free from mercury. The reddish mass is heated in a Hessian crucible with an equal weight of corbonate of soda and about one-fourth as much saltpetre. As soon as the mass is melted, and gas ceases to be generated, it is poured out, so that it may be as much as possible separated from the oxide of lead at the bottom, then dissolved in water which is saturated with sulphuric acid. The sulphate of lead which is precipitated is filtered and the solution treated with hydrochloric and sulphurous acid, by which the selenium is precipitated.

2.

FROM SELENIURETS.

Wöhler has also given the following method for obtaining selenium from the seleniuret of lead. The mineral is pulverised, adhering particles of carbonate of iron and calcspar dissolved in dilute hydrochloric acid, are then entirely removed by washing, and the remaining substance dried, mixed thoroughly with an equal weight of carbonate of potash, containing free carbon or heated bitartrate of potash, and the mixture heated to redness for an hour, with coarsely powdered coal, in a closed crucible.

After cooling, the mass, which now contains all the selenium as seleniuret of potassium, is quickly pulverised in a warm mortar, placed on a filter and treated with hot water, which has been freed from air by boiling, and washed so long as the water is colored. Care must be taken to keep the filter full of water to prevent contact with the atmosphere. The reddish colored solution of seleniuret of potassium begins at once to deposit a film of selenium, so that in a few days all the selenium will be deposited in the form of thin, reddish, black crusts. If a small quantity still remains in the form of selenious acid, it can be precipitated by mixing with hydrochloric and sulphurous acids, and heating.

3.

PREPARATION FROM SOOT. (SELEN RAUCH.)

At a copper furnace in the county of Mansfeld there is deposited, in the high chimney of the roasting furnace, a soot, in considerable quantity, which is black and contains on an average (according to Hofacker) 12% mostly free selenium, together with a large quantity of free sulphuric acid, sulphate of copper, sulphate of iron and coaldust. Arsenic, quicksilver, lead and lime are also contained in very small quantity. The preparation of selenium from this soot is very simple. It is placed on a large filter and treated with water so long as this is colored, and by this means the free sulphuric acid and the salts, soluble in water, are removed. The selenium remains undissolved on the filter, is dried and then distilled in a glass retort covered with a coat of clay. A high heat is necessary to effect the distillation. The melted selenium is received in an appropriate vessel, which, to prevent oxydation, which takes place to a very small extent, may be filled with water. What remains in the retort is selenium in combination with metals. This must be treated with hydrochloric and nitric acids so long as these dissolve any part of it, and then the excess of nitric acid is

expelled by heating, the fluid is diluted, sulphurous acid led into it until it is entirely saturated, then heated, and all the selenium is precipitated. To free it from adhering sulphate of lime it is distilled. To determine the average quantity of selenium in this soot, Traun made use of the following method and obtained the following results. By drying in an airbath at 200° C, the ordinary moist soot lost 27.5% of moisture.

By washing with water 78% impurities were removed. Out of the water used for washing, metallic iron precipitated 8% copper.

The dried and washed soot gave by distilling 39% pure selenium, which shows that in the soot, as it comes from the chimney, $8^1/_2$ % is contained. By dissolving the washed and dried soot in aqua regia and precipitating with selenious acid 34% selenium was obtained and according to this, the original soot would contain 7.75 per cent.

II.

THE SELENIURETS.

In attempting the preparation of these combinations, the leading idea was that if they existed, it was highly probable, that they possessed a similar constitution with the known and analysed sulphurets of the same metals.

1.

SELENIURET OF NICKEL.

As no one had hitherto obtained or described such a combination between nickel and selenium, and since it could be reasonably expected that such a one could be obtained, which would, in all probability, have a constitution similar to that of Millerite, my first efforts were directed to the preparation of such a combination. By the following process I was enabled to obtain one of great interest on account of its peculiar physical properties. According to the atomic weights of nickel and selenium 3.1 grammes nickel would require for forming a simple seleniuret 2.25 gr. selenium, but in case a combination should be formed containing more than one aequivalent of selenium to one of me-

tal, I took 5 gr. of selenium and placed it in one end of a tube of Bohemian glass, which had been closed, and about two inches from the end a little bent to prevent the melted selenium from running along the tube and mixing with the nickel, which was placed about four inches from the end, in a thin layer so as to offer as large a surface as possible to the vapor of selenium which was lead over, after the part of the tube containing the metal had been heated to redness by means of a Liebigs heating apparatus, such as is used for organic analysis. As soon as the vapor came in contact with the metal they combined, with ignition, and the excess of selenium sublimed and was deposited in the cooler part of the tube. The seleniuret thus obtained was a silver white body with dull metallic lustre, which in the atmosphere at the usual temperature is not changed, but, when highly heated, gives off vapor of selenium, and there remains a metallic substance. This body is not changed by water, nor by diluted or concentrated hydrochloric acid. By nitric acid it is slowly dissolved, giving off vapor of nitrous acid. In Aqua regia it is completely dissolved, giving a green solution. At a high, red heat it melts. It is crystalline, and probably belongs to the first system, as some pieces appeared to be tetrahedra, others octahedra, and others again, cubes. It is easily broken into fragments and has an uneven fracture. The specific gravity I found to be = 8.462.

Melted with Borax, in a Hessian tiegel, it gives a beautiful gold-yellow regulus, with radiating lines on the upper surface, while the under surface is crystalline.

Analysis.

By dissolving 1.347 gr. in aqua regia, and precipitating with caustic potash, I obtained .74 gr. protoxide of nickel, which corresponds to .582 gr. nickel. This shows that the substance is a simple seleniuret; since

Ni	29.5	42.88	43.23
Se	39.3	57.12	56.77
		100.	100.

gives a result entirely satisfactory.

The selenium can either be determined by oxidizing by means of chlorine gas to selenic acid, precipitating with chloride of barium and weighing as seleniate of barytes, then calculating the selenium; or it can be precipitated with sulphurous acid, placed on a weighed filter and determined as selenium.

The potash is exceedingly difficult to wash out from protoxide of nickel. The nickel was prepared from oxalate of nickel and ammonia.

Ni Se is not magnetic.

2.
PREPARATION OF SELENIURET OF COBALT.

Berzelius had already found that, „heated cobalt combines with selenium, with ignition, forming a gray mass of metallic lustre, and leafy structure.“

By repeating this experiment in a small glass tube I found that a combination took place, and that by leaving the mass exposed to the air it became blue. In order to obtain a sufficient quantity for the analysis, I took a tube, open at both ends, placed the cobalt in the middle and the selenium near one end, then affixed another tube connected with an apparatus for generating pure hydrogen gas. To obtain this the zink and sulphuric acid used must be free from arsenic. The necessity of leading a stream of hydrogen over the cobalt results from the tendency which this substance has, to oxidize when exposed to the atmospheric air. After the tube was filled with hydrogen and all the air driven out, I heated it, as the nickel in the former case, and a combination ensued with ignition. The generation of hydrogen having been stopped before the selenium was driven over, a part of it had retreated to the end of the tube, and all the cobalt was

not changed. I therefore repeated the operation and led gas over until the change was completed. In this case a combination of selenium with hydrogen was formed, which, when it came in contact with cobalt, was decomposed and hydrogen set free, which ignited spontaneously on coming in contact with the air at the mouth of the tube. An excess of seleniuretted hydrogen, which was formed, issued from the end of the tube and gave me an opportunity of testing the correctness of the statement of Berzelius in regard to the danger of inhaling this disagreeable gas. In odor it resembles sulphuretted hydrogen, and directly after smelling it, there follows a painful pricking sensation in the mucous membrane of the nostril, which resembles that which boys experience on biting an unripe persimmon, Diospyros Virginiana, before frost.

There is also a tickling or irritation in the throat which induces coughing. The sense of smell is entirely destroyed for several hours so that one can hold concentrated ammonia to the nose without the slightest inconvenience.

The great Swedish chemist, after smelling it, was affected with a severe cough, which lasted 14 days; but this must have been owing either to his nice sense of smell, or to his having a bad cold at the time, as I felt no inconvenience from it, on the next day after inhaling it.

By very high heat in a tube this seleniuret of cobalt can be melted. With borax I obtained a crystalline regulus, of yellow (speissgelb?) color, laminated

and in some small crevices, beautiful blue laminae were found. It is very easily reduced to a beautiful brass-yellow, shining powder. Fractured, it is uneven and granulous.

In hydrochloric acid a small quantity of excess of selenium is dissolved and seleniuretted hydrogen is given off, and afterwards on standing, some selenium is deposited on the bottom. In nitric acid, at the usual temperature it is slowly dissolved, by warming, very quickly, and nitrous acid is set free.

Analysis.

By dissolving in nitric acid and precipitating with caustic potash, I obtained from .828 gr. substance 442 gr. protoxide of cobalt, which corresponds to .347 gr. Co

Co	29.5	42.88	42.31
Se	39.3	57.12	57.69
		100.	100.

The Selenium can be determined in the same way as before. Spec. grav. = 7.647.

3.
SELENIURET OF IRON.
PREPARATION.

This has been already prepared and its physical properties described fully by Berzelius, it is only necessary for me to recapitulate the results of his experiments and to explain how I obtained it in sufficient quantity for analysis. He says: „The vapor of selenium led over iron filings unites with them with ignition. By heating iron filings with powdered selenium, the combination is imperfect, and there is no appearance of fire. It is yellowish gray, of metallic lustre, hard, brittle, with granular fracture, heated alone, not fusible, but baking together. Melts before the blowpipe, with generation of oxide of selenium, to a black, brittle ball, with conchoidal fracture, which appears to be selenide of iron. It is soluble in hydrochloric acid, with development of seleniuretted hydrogen. If air be present, the fluid is turgid through selenium, which is deposited; at the same time is generated another gas, of very disagreeable odor, which is neither absorbed by water, nor by alkaline solution, and gives a black precipitate with Hg^2O, NO^5.

Powdered seleniuret of iron is converted by heating with more selenium into a brownish powder, which is insoluble in hydrochloric and by high heat loses selenium."

By leading selenium vapor over fine iron wire, I obtained, without change in the form of the wire, a combination, which is very brittle. This was probably simple seleniuret. I melted a quantity of this with excess of selenium in a Hessian crucible with borax, and obtained a regulus which was grayish-yellow, had uneven fracture, was very easily pulverised, and indeed by exposure to the air was easily disintegrated. With water it gives a brown-red color, which seems to come from seleniuret of natrium, formed from the borax, and adhering to the regulus. With dilute and concentrated hydrochloric acid it gives a solution of sesquichloride of iron. Treated with dilute nitric acid, the horse-radish odor of seleniuretted hydrogen could be recognised. Concentrated nitric acid gave a yellow solution. This was also the case with aqua regia.

Analysis.

A piece weighing .587 gr. was dissolved in nitric acid, and the hydrate of the sesquioxide of iron was precipitated; after driving off the water, it gave .273 gr., which corresponds to 191 gr. of metallic iron, and gives for the chemical formula Fe_2Se_3 which corresponds to the sesquioxide.

2Fe	56	32.20	32.15
3Se	117.9	67.80	67.85
	173.9	100.	100.

The spec. grav. = 6.38.

4.
SELENIURET OF CADMIUM.

Cadmium not having been discovered at the time when Berzelius was engaged in investigating the seleniurets, he never had an opportunity of working with this combination.

A small piece of cadmium was heated in a glass tube with selenium and there resulted a combination with generation of heat and strong light. By higher heat cadmium appeared to be sublimed to a cooler part of the tube. On repeating the experiment with a larger quantity, the action was so violent that a hole was blown through the end of the tube, out of which a brown vapor issued. On making the experiment in the same way as with the cobalt and nickel, I obtained gold-yellow globules of metallic lustre, and, after the melting body had cooled, a crystalline structure was very apparent. During the operation the odor of burning leather was given off. The selenium remained in a soft tenacious state. The end of the tube was blown out as in the other case. By melting a portion with borax, I obtained a grayish black regulus, laminated and crystalline, which had exactly the appearance of

zincblende, and, in a small cavity, I noticed the perfect impression of the end of a six sided prism. This compound is very easily pulverised and is blackish gray. In hydrochloric acid it is scarcely soluble, and gives off seleniuretted hydrogen. By the addition of nitric acid, there appeared a brown coloring of the solution, which disappeared almost immediately, and could not be brought out again. In aqua regia, it is easily soluble, and gives a clear solution, out of which carbonate of soda precipitates white carbonate of oxide of cadmium. .284 gr. of seleniuret of cadmium gave .183 gr. oxide of cadmium which gave .161 gr. metallic cadmium and from this we find the formula Cd Se.

Cd	55.7	57.57 found	56.76
Se	39.3	43.43	43.24

Spec. grav. 8.789. It is a curious circumstance that Cd Se cannot be sublimed, although both of its components can be.

5.
SELENIURET OF TIN.

According to Berzelius, tin combines with selenium, by heating, with ignition, to a gray material, of metallic lustre, which, exposed to the air and heated, is decomposed without melting, into selenium, which sublimes, and oxide of tin, which remains.

By precipitating cloride of tin with seleniuretted hydrogen double seleniuret of tin can be formed. By putting tin foil in a tube and heating, it is at first united to a scaly conglomerated mass, then melted, and when vapor of selenium is driven over it, ignition takes place. As not enough selenium had been taken to combine with the whole amount of tin, all of the former was absorbed, and entered into combination, showing the strong tendency to unite, which exists between these two elements. The compound which resulted was a beautiful, tin-white mass, with bright metallic lustre on the surface and conchoidal fracture. It melts quite easily, is easily separated into laminae. In dilute and concentrated hydrochloric acid it is not affected, in nitric acid easily decomposed, and per-

oxide of tin remains undissolved. In hydrochloric and nitric acid together, very easily dissolved.

Analysis.

By dissolving .41 gr. of seleniuret of tin in aqua regia and precipitating with caustic potash I obtained .228 gr. peroxide of tin which gives .179 gr. metallic tin and shows that the formula for this compound is $Sn\ Se_2$ and therefore corresponds to the peroxide of tin.

		calculated	found
Sn	58.8	42.79	43.71
2Se	78.6	57.21	56.28
		100	100

The specific gravity is 5.133.

6.
SELENIURET OF BISMUTH.

We find also a notice, of the action of bismuth with selenium, by Berzelius. He says that the two substances unite by heating, with ignition, to a silver-white mass with crystalline fracture. Heated to redness, the mass melts, and the surface reflects like a mirror. I found also that they boil when heated together, and the mass on cooling exhibits a very fine laminated structure.

The combination is not affected by hydrochloric acid, either dilute or concentrated. In dilute nitric acid, it is somewhat, and in concentrated, easily and completely, soluble, also in aqua regia. Before the blowpipe, selenium is sublimed, and there is left on the coal the brown-yellow coating of oxide of bismuth. It is easily separated into laminae, and with difficulty reduced to a gray powder. By dissolving 768 gr. in nitric acid, then precipitating, with carbonate of ammonia, the carbonate of bismuth, and heating, to prevent the solution of the precipitate, in excess of the carbonate of ammonia, and then heating the carbonate to drive off carbonic acid, I obtained .57 gr. oxide of bismuth, which corresponds to .511 gr. metallic bismuth. This gives for the formula of the seleniuret $Bi\,Se_3$ since

Bi	208	63.82	66.79
3Se	117.9	36.18	33.21
		100	100

The specific gravity is 7.406.

7.

SELENIURET OF COPPER.

Subseleniuret of copper or Berzelianite of Dana occurs native. It can also be obtained by heating copper with selenium, or by heating to a high degree simple seleniuret in a closed vessel. It is dark steel gray, in the form of thin dendritic crusts, and melts below the point of ignition. Loses by continued heating, exposed to the air, only a part of its selenium, gives off a horse-radish odor, and leaves gray, brittle, easily fusible copper.

2Cu	64	61.54	64 (from Smoland.)
Se	40	38.46	40 (Berzelius.)

Simple seleniuret of copper is obtained by precipitation of sulphate of copper by means of seleniuretted hydrogen in the form of black, flakes, which become, by drying, dark gray and receive, by polishing, a metallic lustre. Loses by sublimation half of its selenium.

By leading selenium vapor over sheet copper I obtained a greenish, black, crystalline, globule which showed a play of colors on the surface, and when heated before the blowpipe on charcoal, gave off finely divided red selenium, and the copper sank into the coal. In dilute, as also in concentrated heated, hydrochloric

acid, it is little soluble. In heated nitric acid is easily and completely soluble. The solution is blue.

Analysis.

I dissolved .35 gr. in aqua regia and after diluting precipitated with caustic potash. The hydrated oxide was boiled and reduced, to oxide = .195 gr. which gives .154 gr. metallic copper and hence we have the formula CuSe

Cu	31.7	44.64	44.03	50.
Se	39.3	56.36	55.97	50.

The specific gravity is 6.655.

8.

SELENIURET OF QUICKSILVER.

Berzelius says that the two substances Se and Hg unite by heating without giving off light. a. If excess of quicksilver be used, and that which does not enter into combination be driven off, there remains a tin white, firm compound, which sublimes, without melting, in crystals of metallic lustre. b. By heating quicksilver with an excess of selenium, the latter is at first sublimed, then a gray, indistinctly crystalline substance which is either seleniuret of quicksilver in maximum, or a mixture of (a) and selenium. Seleniuret of quicksilver is easily dissolved in aqua regia to selenite of oxide of quicksilver. Only by continued boiling with nitric acid is it changed into selenite of suboxide, which is in the form of a white powder, while some selenious acid is dissolved in the nitric acid. My first experiment was to heat Se and Hg in a tube. They combined, with a crackling noise, to a compound, which can be sublimed in crystals of the monometric system, with a surface reflecting purple or violet.

A second experiment with quicksilver in a retort with red selenium powder, mixed with gypsum, gave

also crystals, and a black powder. By heating Hg. Se. with iron filings, seleniuret of iron is formed, and quicksilver is deposited, in the shape of small globules on the tube. The powder of seleniuret of quicksilver, mixed with hydrate of potash, is black, and not red, as is the case with the sulphur combination. By friction the odor of selenium is given off. Hg Se is entirely volatile before the blowpipe, and burns with a blue flame.

In diluted and concentrated hydrochloric acid it is not soluble, in nitric acid slowly, and in aqua regia very easily.

By dissolving 0.916 gr. and treating with sulphuret of ammonium the selenium was held in solution while the quicksilver was precipitated as Hg S = 0.890 which gives metallic quicksilver = .767 and the formula = Hg_2Se

2Hg	200	83.62	found 83.76
Se	39.3	16.38	16.20
		100	100

The specific gravity is equal to 8.877.

9.

SELENIURET OF LEAD.

Is found native as a mass very similar to Galena and is called by Dana Clausthalite. Berzelius says that lead unites with selenium, with ignition, forming a gray porous soft mass, which by polishing becomes white. The compound heated in an open vessel gives off, without melting, at first some selenium, then seleniuret of lead in white fumes. Before the blowpipe, on charcoal, it gives off selenium, colors the flame blue and deposits a reddish brown substance, then suddenly sinks into the coal, leaving a coating of seleniuret. It is changed into basic selenite of lead. Cold nitric acid dissolves the lead, while selenium is deposited, which is by degrees also dissolved, and forms selenious acid. The powder gives with sulphuric acid, at first, a brownish, then greenish, then reddish-brown mixture. By mixing water to the green solution a beautiful red color is produced. Melted with borax and glass, a portion of it gave small crystals, belonging to the monometric system. With borax alone, I obtained a firm Regulus, which was oliated, crystalline, steel gray, easily reducible to powder fand on the outer surface, variegated.

In dilute and concentrated hydrochloric acid with difficulty, in nitric, tolerably easily dissolved. In aqua regia easily, and completely dissolved. The softness that Berzelius observed in this compound, was probably due to excess of selenium, as the mass that I obtained was quite firm. By treating a solution of this substance in nitric acid with sulphuret of ammonium, the lead is precipitated, and sulphuret of selenium remains in solution. Sulphuret of lead is dissolved, and precipitated as carbonate. .718 gr. gave .55 gr. oxide of lead = .51 gr. metallic lead.

			Tilkerode H. Rose	Clausthal Stromeyer	artificial
Pb	104	72.72	71.81	70.98	71.
Le	40	27.28	57.59	28.10 .83?	28.

Spec. gravity of the artificial 8.154.

10.

SELENIURET OF ARSENIC.

Melted selenium dissolves, by degrees, arsenic, and forms a black, easily fused mass, which boils, when heated to redness, and seleniuret of arsenic in maximum appears to be given off. Thereupon the boiling ceases, and only when brought to a white heat, the whole mass forms drops, which on cooling harden to a brownish black mass with metallic lustre and conchoidal fracture. Berzelius. Before the blowpipe it is entirely sublimed and gives off at first a horse-radish odor from the selenium, and then an alliaceous odor from the arsenic. It is very brittle, and easily reduced to a black powder, of metallic lustre. Dilute hydrochloric acid does not produce any effect upon it. Concentrated, when heated, dissolves it slowly. Diluted and concentrated nitric acid also produces scarcely any change.

In hot aqua regia it is tolerably easily dissolved.

Analysis.

In this case I used the method given by Rose for separating tin, antimony, and arsenic from selenium. The selenium was first precipitated from a solution of .642 gr. in aqua regia, by driving out first all the

nitric acid, then leading a stream of sulphurous acid gas into the solution, until after boiling no farther red color, was produced by adding SO_2. The solution saturated with SO_2 was boiled until all the selenium was deposited as a black mass.

This gave when dried and weighed .365 gr. = 57 %.

The arsenic which remained in solution was precipitated as arseniate of ammonia and magnesia = .7 gr. which gives metallic arsenic = .276 gr. or 43.83 %.

As	75	38.94	found	57.00
3Se	117.9	61.06		43.03
		100		100.03

The specific gravity = 4.752.

SELENIUM AND ANTIMONY.

Hofacker (in his Inaugural Dissertation Gött. 1857.) explains the process, which he employed to form two combinations of these bodies, one corresponding to the oxide of antimony, and the other to the antimonic acid. The first he obtained by melting one equivalent of antimony (3 grammes) with three equivalents of selenium (3 grammes) in a porcelain capsule. A small loss of selenium could not be avoided. He obtained a lead gray, metallic mass, which in fracture nearly resembled antimony glance.

Heated in the outer blowpipe flame the penetrating odor of selenium was given off, and white fumes of antimonious acid were formed.

The higher seleniuret $SbSe_5$ he obtained by dissolving $3NaSe + SbSe_5 + 18HO$ in water which had been freed from air by boiling, then decomposing the solution with hydrochloric acid. Seleniuretted hydrogen is set free. The pentaseleniuret of antimony, which was precipitated, is a brown powder, which by heating loses selenium, and becomes gray and crystaline. In caustic potash it is soluble. He dissolved it in aqua regia, drove off the nitric acid and precipitated selenium with sulphite of ammonia.

As the result of his analysis he found that there were contained in the substance five equivalents of selenium and one of antimony

Antimony	139.	37.5	34.5
5 Selenium	196.5	62.5	63.4
		100	97.9

III.
ISOMORPHISM OF SELENIUM AND SULPHUR.

Mitscherlich who discovered the law of isomorphism, after observing the fact that the arseniate and phosphate of soda, which have a similar chemical constitution, have also the same forms of crystallisation, was also the first, who directed attention to the fact, that the sulphate and seleniate of potash possess the same property. The acids of sulphur and selenium are also considered isomorphous, although crystals of selenic acid have not yet been obtained. The sulphurets and seleniurets of lead and silver are also isomorphous. Mitscherlich has shown that sulphur and selenium are not only isomorphous but dimorphous. That is, they each crystallise in two distinct forms, which are common to both.

The Onofrite of Haidinger is a combination of quicksilver with sulphur and selenium, in which one equivalent of the former is replaced by one of the latter, which gives the formula $HgSe + 4HgS$.

The „natrium-sulfo-selen-antimoniat“ of Hofacker is a salt which has the formula $3NaS + Sb\left.\begin{matrix}S_3\\Se_2\end{matrix}\right\} + 18HO.$ in which two equivalents of selenium are replaced by two of sulphur. We see from these examples how interesting this law of isomorphism is for chemistry as well as for mineralogy.

IV.
SIMILARITY OF THE COMBINATIONS OF OXYGEN, SULPHUR AND SELENIUM.

No one, who has been engaged in the study of chemistry for any length of time, can fail to have noticed that the elements can be divided into groups, the members of which often resemble each other very nearly in physical properties, in form and in their behavior toward other substances. There can also be traced certain relations between the equivalent numbers of these groups, which, though not yet sufficiently studied to be of any practical benefit, are still highly interesting. Thus for instance Dumas has called attention to the fact that the equivalent number of selenium is the mean of those of sulphur and tellurium or

16 : 40 :: 40 : 64.

We find that wherever sulphur enters into combination with another element, there is, in almost every case, a corresponding oxygen compound. Thus we have an oxide, a protoxide and a sesquioxide of iron which, in the sulphur series, are represented by the sulphuret, bisulphuret and sesquisulphuret. That the

same is true of selenium ean be seen from the following review of the results of my analyses.

NiO	CoO	Fe_2O_3	CdO	SnO_2	BiO_3	CuO
NiS	CoS	S_3	S	S_2	S_3	CuS
NiSe	CoSe	Se_3	Se	Se_2	Se_3	CuSe

PbO	HgO	AsO_3	SbO_3	SbO_5
PbS	S	S_3	S_3	S_5
PbSe	Se	Se_3	Se_3	Se_5.

Our substance belongs therefore in the group which contains oxygen and sulphur, to which tellurium may also be added.